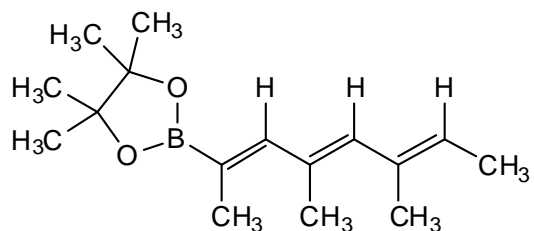


**In-Class Exercise:
Through-Space Correlations with 2D NOESY**

Susan Brown (Hoye group) needed to synthesize the trienyl boronate at right with perfect retention of alkene stereochemistry; isomerization of any of the (*E*)-alkenes to (*Z*) stereochemistry under her reaction conditions would represent a failed synthesis. (I left out the details of the synthesis, because they're

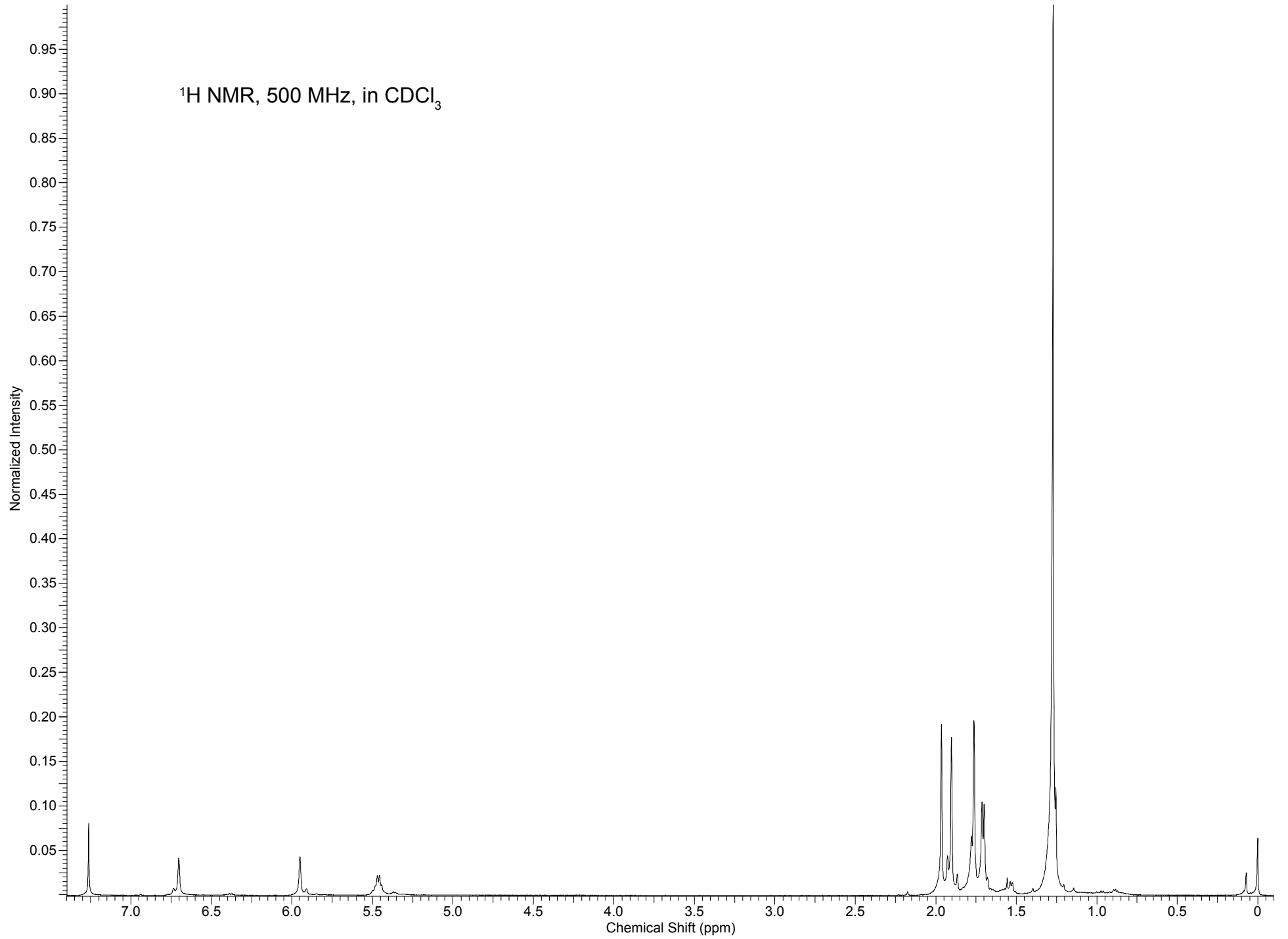


not important for interpreting her NMR spectra.) Because there was so little ^1H - ^1H coupling in her reaction product, Susan couldn't analyze the molecule using scalar coupling methods, and had to use through-space correlation spectroscopy instead.

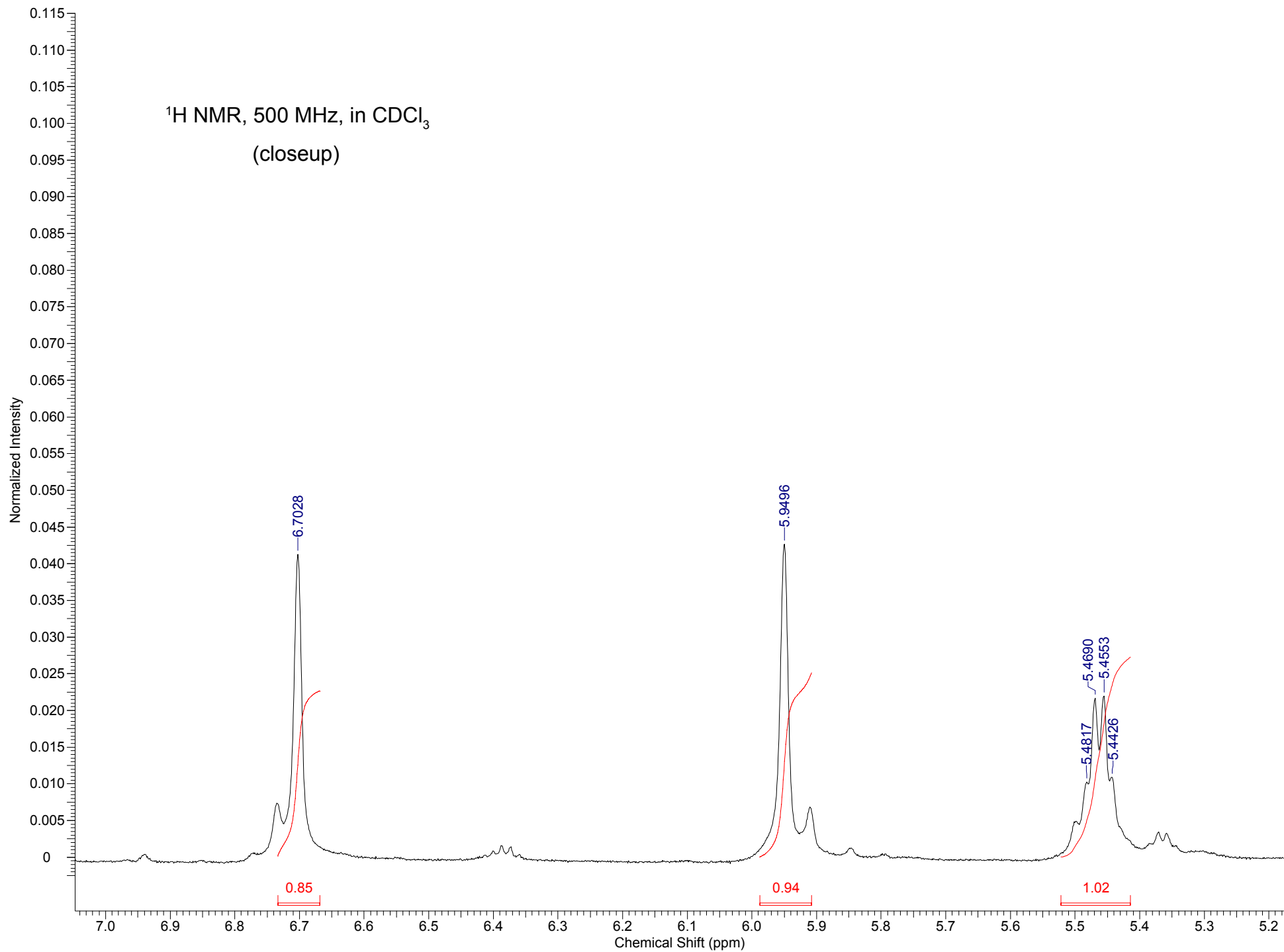
1D ^1H and 2D ^1H - ^1H NOESY spectra of Susan's isolated product are shown on subsequent pages.

- I have drawn the two central single bonds of the triene in their *s-trans* conformation, but the barrier to rotation about each single bond is only ~ 5 kcal/mol, and at room temperature each single bond is expected to assume its *s-cis* conformation some of the time. Given this, what through-space "neighbor" relationships would you expect to see for each proton in the structure above?
- Assign chemical shifts to each proton in Susan's product. Are there any peaks that you still can't assign?
- Is the NOESY spectrum consistent with the (*E*)-alkene stereochemistries shown above, or could Susan's product contain (*Z*)-alkenes instead?

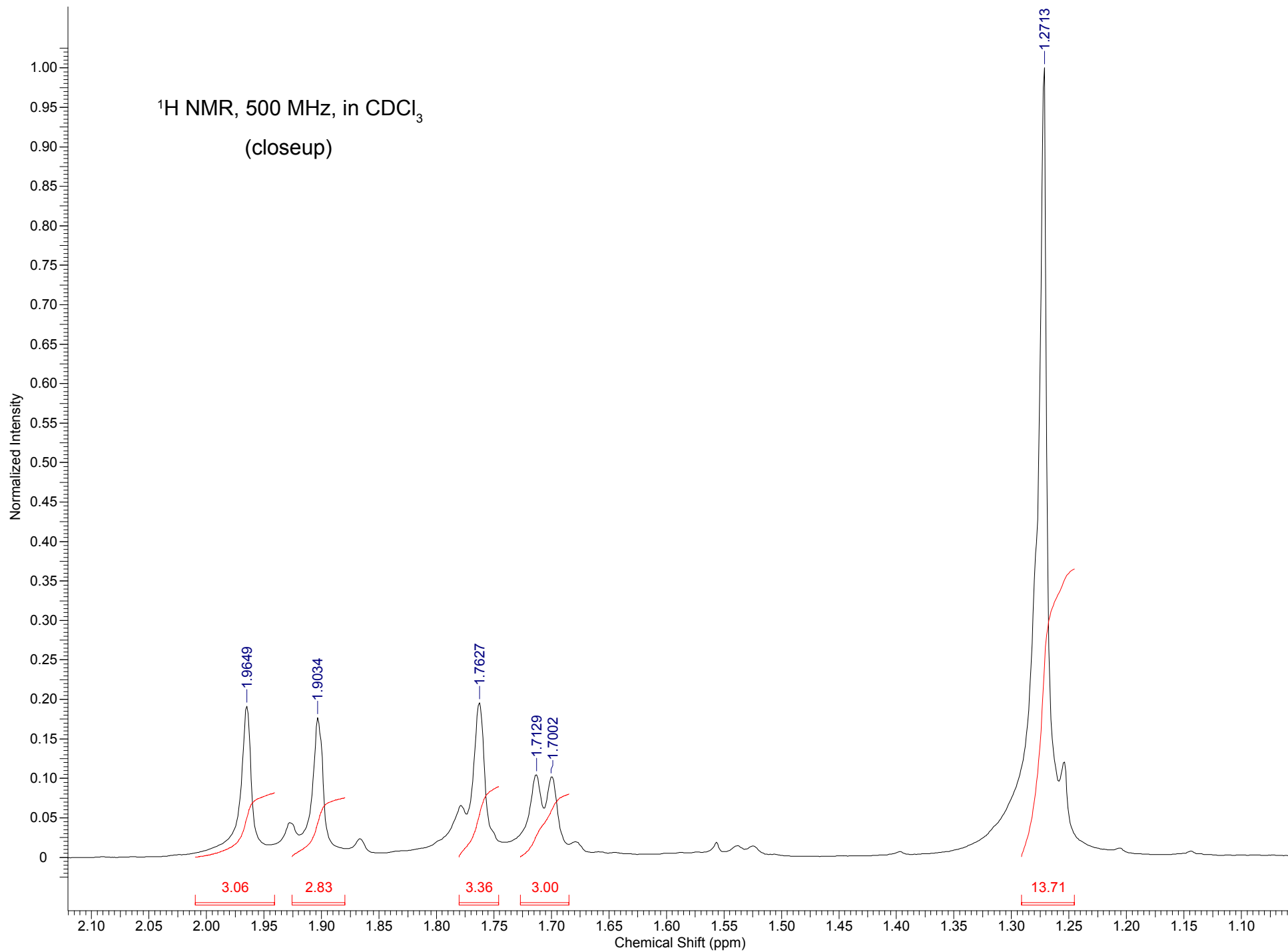
^1H NMR, 500 MHz, in CDCl_3



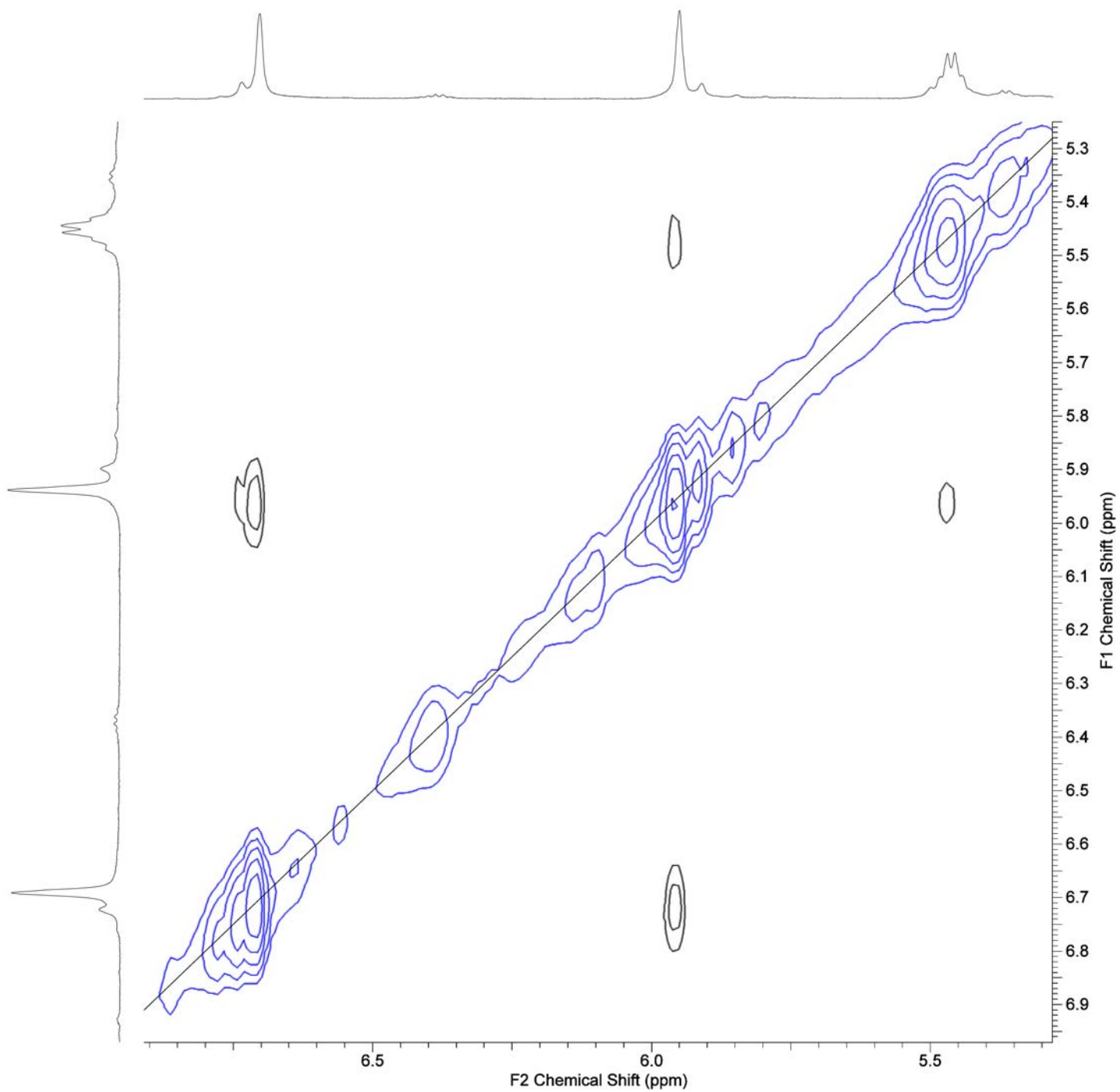
^1H NMR, 500 MHz, in CDCl_3
(closeup)



^1H NMR, 500 MHz, in CDCl_3
(closeup)



^1H - ^1H NOESY, 500 MHz, in CDCl_3
(closeup)



^1H - ^1H NOESY, 500 MHz, in CDCl_3

(closeup)

